Spectroscopic Studies of Diatomic Gallium Halides

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An extensive study of the available spectroscopic information on four gallium monohalides has been conducted. The literature survey extends to early 2003 and the experimental and theoretical data on the molecular constants for the ground state, as well as for the excited states of these molecules, is presented. A brief discussion on the spectroscopic properties of different electronic states, ionization potentials, ground state dissociation energies, and percentage ionic character are given. The Rydberg–Klein–Rees potentials for the electronic states and centrifugal distortion constants for the observed vibrational levels for the electronic states of GaX (X=F, Cl, Br, and I) are also presented. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1797791]

Key words: diatomic gallium halides; dissociation energy; ionization potential; molecular spectroscopic constants.

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1. Introduction

Metal halide vapor show many physical and chemical properties that make them attractive as possible laser medium.[1–4] Ultraviolet (UV) photodissociation of heavy IIIA group monohalide molecules has turned out to be a very effective pumping process for atomic resonance laser action in one of the photofragments. Recently new emission spectra reported by Venkatsubramanian *et al.*,[5] has indicated the prospects of gallium monohalide molecules as an efficient excimer laser system. The gallium monohalides play an important role as intermediates in the production of new high-frequency and opto-electronic semiconductor devices.[6] GaCl has practical importance in the manufacture of advanced GaAs semiconductor devices where gas-phase chlorinated reagents are used commonly to modify the GaAs surface.[7–9] Studies of chemical vapor deposition also indicate that gas-phase GaCl can deposit gallium atoms on to a GaAs surface.[10] All these application oriented studies have emphasized the need for basic data on the spectroscopic properties of these monohalide molecules.

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Spectroscopic investigations on the diatomic halides of gallium have been the subject of much interest for a long time.[11–19] The general behavior of the spectrum of gallium monohalides is very similar to the one described for indium monohalides.[1] Three low lying electronic states $A\,^3\Pi_0$, $B\,^3\Pi_1$, and $C\,^1\Pi_1$ are known through transition to the ground state $X\,^1\Sigma^+$ in all these molecules. Rydberg states are also reported only for GaCl. This group of IIIA group monohalides is amongst the least studied (until 1990) from the spectroscopic view point due to the presence of two equally abundant isotopes of Ga which results in a complex structure. However, recently a number of theoretical and experimental works on the electronic spectrum of these molecules have been reported.

In 1933, Partrikaln and Hochberg[11] first observed the electronic spectrum of the GaCl radical. Miescher and Wehrli[12,13] recorded the electronic band spectrum of GaCl, GaBr, and GaI in both emission and absorption. This proved the stability of gallium monohalides in the gas phase and these authors determined the molecular constants for the ground as well as for the low lying excited states ($A\,^3\Pi_0$ and $B\,^3\Pi_1$) of these molecules. They also identified an additional excited ($C\,^1\Pi_1$) state. About 2 decades later Levin and Winans,[14] Welti and Barrow,[15] Barrow *et al.*,[16,17] and Bartky[19] reanalyzed the spectra of diatomic gallium halides. Later, Savithry *et al.*,[20] Lakshminaryana and Sethumandhavan,[21] Borkowska and Zyrnicki,[22] and Griffith *et al.*[23] extended the work on the electronic spectrum of these molecules at an improved resolution. Recently, Mahieu *et al.*,[24] Borkowska and Zyrnicki,[25–27] and Saksena and co-workers[28–31] reported further studies at high resolution.

Grabandt *et al.*[32] investigated the photoelectron spectra of gallium monohalide molecules. They have also carried out the Hartree–Fock–Slater (HFS) type density functional theory (DFT) calculations with a pseudopotential technique on these molecules. Dearden *et al.*[33] reported the resonance enhanced multiphoton ionization (REMPI) spectra of GaCl and they have assigned five Rydberg series involving 20 new electronic states reported for the first time. Balasubramanian and co-workers[34,35] investigated the electronic structure of GaCl and GaBr molecules with *ab initio* complete active space multiconfiguration self-consistent field (MCSCF) (CASSCF) calculation followed by the method of first and second order configuration interactions. Yoshikawa and Hirst,[36] Kobus *et al.*,[37] Mochizuki and Tanaka,[38] and Bauschlicher[39] performed further theoretical studies on the electronic structure of these molecules. Recently, Dutta *et al.*[40] have calculated the potential energy curves and spectroscopic constants for the low-lying electronic states of gallium monoiodide by the method of multi reference single and double configuration interaction (MRDCI) based on relativistic effective core potential. They also estimated the radiative lifetime of the $^3\Pi$ states from the transition probability data for the first time. Most recently Yang *et al.*[41] calculated the spectroscopic constants of the ground state as well as the low-lying excited states of GaX (X=F, Cl, Br, and I) molecules using the DFT. In this work, different local density approximations (LDAs) and general grading approximations (GGAs) and relative relativistic correction are used to perform the total energy computation for these molecules. Most recently, an *ab initio* study of the ground and valance excited states including spin orbit coupling effects of GaCl have been performed by Yang *et al.*[41b] The transition properties of low lying excited states are predicted. A high resolution infrared emission on $\Delta v=1$ bands was reported by Uehara *et al.*[42] First measurements of pure rotational transitions of gallium monohalides GaCl, GaBr, and GaI were done by Barrett and Mendel.[43] Further microwave spectral studies on the gallium monohalides have been carried out by a number of researchers.[44–56] Most recently, Lenthe *et al.*[57] performed DFT calculations to evaluate nuclear quadrupole coupling constants of a number of metal halide molecules, including the GaX molecules.

Recently, more theoretical work for the GaX molecules have been performed (which were lacking in the case of InX molecules). However, more experimental work for the InX molecules is reported in comparison to GaX molecules. In both groups of molecules, the five low lying excited bound Ω states: $^3\Pi_0^-$, $A\,^3\Pi_0^+$, $B\,^3\Pi_1$, $^3\Pi_2$, and $C\,^1\Pi_1$ are generated. Only the transition from $A\,^3\Pi_0^+$, $B\,^3\Pi_1$, and $C\,^1\Pi_1$ states to the ground state $X\,^1\Sigma^+$ are allowed (as shown in Fig. 1 in Mishra *et al.*[1]) and have been observed in the experiment. In all diatomic halides of gallium and indium, the $A-X$ and $B-X$ transitions are very strong and lying in the UV-visible region. The electronic spectrum of diatomic halides of gallium are slightly shifted towards shorter wavelength sides in comparison to the corresponding halides of indium. The dissociation energy of both groups of the molecules follows the same trend, the D_e values decrease with the increasing mass of the molecule. The atomic dissociation product for $C\,^1\Pi_1$ state for most of these molecules turns out to be $M^*\ (^2P_{3/2})+X(^2P_{3/2})$. The percentage of ionic character slightly increases in the ground states of the gallium monohalides molecules in comparison to corresponding indium monohalides. The $C\,^1\Pi_1$ state in both indium and gallium monohalides becomes progressively less stable as the mass of the halogen increases. The analogy in the Rydberg state assignments between GaCl and InCl was found to be limited.

In the present paper, we have attempted to summarize the available spectroscopic information about gallium monohalides. A brief discussion on the spectroscopic properties of different electronic states, ionization potentials, ground state dissociation energies, and percentage of ionic character are given. The review is arranged in following manner. Section 2, consisting of four subsections, covers the ground state properties as exemplified by

(1) the results of quantum mechanical calculations of electronic structure (Sec. 2.1),
(2) the photoelectron spectra (Sec. 2.2),
(3) the dissociation energy (Sec. 2.3), and
(4) the calculated percentage ionic characters (Sec. 2.4).

In Sec. 3, the results of the studies on the microwave spectra of gallium monohalides are summarized. The spectroscopic

properties for the low-lying excited states are discussed in Sec. 4. In Sec. 5, the available information about the Rydberg states and states of corresponding molecular ions is summarized. Finally, the conclusions and suggestions for further study are described in Sec. 6.

2. Ground State

2.1. Nature of Bonding in the Ground State

The ground state of all gallium monohalides is of the $^1\Sigma^+$ (or 0^+ in case c) type, similar to other diatomic molecules formed by IIIA group elements (e.g., B, Al, Ga, In, and Tl) with halogens (e.g., F, Cl, Br, and I). In many cases this has been verified by experimental observation of the rotational structure and also by theoretical calculations. Recently *ab initio* based MRDCI calculations on GaI molecule reported by Dutta *et al.*[40] and most recently *ab initio* study of the ground state of GaCl reported by Yang *et al.*[41b] also reveal that the ground states of GaI and GaCl are $^1\Sigma^+$ type. The singlet ground state $^1\Sigma^+$ of gallium monohalide molecules are generated by the following ground state electronic configuration:

$$\sigma_1^2\sigma_2^2\sigma_3^2\pi_1^4.$$

This ground electronic configuration arises from the interaction of the ground state Ga (^2P, $4s^24p^1$) with the ground state of the halide atom X (^2P, ns^2np^5, $n=2$, 3, 4, 5). The outermost p shells of gallium and halogen atoms are active. It has been found that $3d^{10}$ electrons in Ga and nd^{10} electrons of the heavier halogen do not participate actively in the formation of the Ga–X (=F, Cl, Br, and I) bond.

Recently number of *ab initio* studies on these molecules were reported. Grabandt *et al.*[32] have performed HFS calculations for these molecules and concluded that the highest occupied molecular orbital (MO) is largely on Ga in GaF (60% Ga 4s; 10% Ga 4p_z; 30% F 2p_z) which but in GaI, the contribution of Ga and the halogen become almost equal (30% Ga 4s; 20% Ga 4p_z; 50% I 5p_z). *Ab initio* calculations for the ground and the first electronic excited state of GaCl and GaBr molecules have been carried out by Balasubramanian and co-workers.[34,35] They have described that in the case of the GaBr molecule the σ_3 molecular orbital is predominately Ga(4s), while the σ_2 and π_1 are predominantly Br(4p). Most recently, Yang *et al.*[41] conducted *ab initio* DFT calculations for all gallium monohalides. These density functional theory calculations show that the outermost p shells of gallium and halogen atoms are active.[41] On the basis of the photoelectron spectra and *ab initio* HFS calculations for gallium monohalides the following brief conclusion about the nature and bonding character of the outermost molecular orbital in these molecules are presented.

(i) The outermost σ orbital has mainly Ga character but halogen character increases as we go from F to I.

(ii) The doubly degenerate π orbital is of predominately halogen lone pair character.

(iii) The next inner MO is another σ MO. It is mostly a $np\sigma$ orbital centered on the halogen atom, with only a small contribution from $ns\sigma$ of the Ga.

Thus, we conclude that the nature and bonding character of outermost molecular orbitals in GaX molecules are very similar to InX molecules.[1]

2.2. Photoelectron Spectra

Photoelectron spectroscopy (PES) has been used extensively as a suitable method for obtaining information about the electronic structure of neutral and ionic states of diatomic molecules in the gas phase. Despite their short-lived character several group III monohalides have been the subject of PES studies.[6,58–64] Berkowitz,[59] Berkowitz and Dehmer,[60,61] Egdell *et al.*,[62] and Grabandt *et al.*[6] have carried out investigations on the photoelectron spectroscopy of indium and thallium monohalides in the gas phase and observed, in general, three peaks in the photoelectron spectra of each of these molecules. The peaks were interpreted to involve ionization from the three outermost molecular orbitals leading to the formation of molecular ions in three different low lying electronic states $X\,^2\Sigma$, $A\,^2\Pi$, and $B\,^2\Sigma^+$. These studies all show that the chemical bonding throughout the series of group III monohalides is predominantly ionic rather than covalent in nature.

He(I) PES of the short-lived gallium monohalides, produced via a new solid state reaction, have been recorded and interpreted on the basis of the *ab initio* Hartree–Fock–Slater calculations by Grabandt *et al.*[32] The solid state reactions, in which the title compound can be generated in the gas phase in significant concentrations in the virtual absence of other species, have been shown to produce a successful approach for PES. Three ionic states of all four gallium monohalides have been identified in this paper[32]

The first peak in the photoelectron spectrum of GaF appears between 10.5 and 11.0 eV and attributed to the transition from the neutral ground state ($X\,^1\Sigma^+$) to the lowest ionic state ($X\,^2\Sigma^+$). This band shows five components and the distance between first and second component is found to be $\sim 605\ \mathrm{cm}^{-1}$ which corresponds to the vibrational frequency associated with the neutral ground state. The vibrational progressions associated with the lowest ionic state were also observed in the above first band with a vibrational spacing of $\sim 745\ \mathrm{cm}^{-1}$. This shows an increase in the vibrational frequency in the ionic ground state ($X\,^2\Sigma^+$) in comparison to neutral ground state ($X\,^1\Sigma^+$) of GaF. The adiabatic ionization energy corresponds to the lowest ionic state is found to be 10.64 eV. The second peak, which is quite broad, was observed between 12.9 and 14.5 eV. This band does not show any resolved structure. The structureless third peak was observed between 15.0 and 15.8 eV with low intensity. Similar three peaks were also observed for the other gallium monohalides.

Grabandt *et al.*[32] have calculated the potential energy curves using the HFS method for the neutral ground state

TABLE 1. Experimental and theoretical ionization energies (in eV) for gallium monohalides

State of ion	GaF		GaCl		GaBr		GaI	
	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical
$X\ ^2\Sigma$	10.64[a,b]	10.45[a]	9.91	9.64	9.59	9.23	9.03	8.60
	10.74[b,c]	10.45	10.07	9.68	9.72	9.23	9.19	8.60
$A\ ^2\Pi_{1/2}$	12.91[d,e]	—	10.81	—	10.14	—	9.93	—
	13.61[c,e]	13.69[c]	11.38	10.82	10.60	10.24	10.25	9.64
$A\ ^2\Pi_{3/2}$	12.91[d,e]	—	10.80	—	10.14	—	—	—
	13.61[c,e]	13.65[c]	11.38	10.74	10.60	9.88	9.49	8.94
$B\ ^2\Sigma^+$	15.07[d,e]	14.17[a]	—	13.53	13.45	13.40	12.81	13.03
	15.41[c,e]	15.16[a]	14.05	13.59	13.62	13.44	12.98	13.03

[a]Adiabatic transition.
[b]± 0.01 eV.
[c]Band maxima.
[d]Band onset.
[e]± 0.04 eV.

and three low-lying ionic states of the gallium monohalides. From the computed potential curves the adiabatic and vertical ionization energies for the ground state of GaX (X=F, Cl, Br, and I), as well as for the three ionic states of GaX, have been obtained. The experimental and calculated ionization energies for all these diatomic halides are given in Table 1. A comparison of calculated and experimental values of equilibrium bond lengths, associated vibrational frequencies and their anharmonicities are given in Table 2.

The photoelectron spectra and HFS calculations shows that the ground states of gallium monohalides ions are bound states and the internuclear separation in the ion is slightly less than for the corresponding neutral GaX (ground states). The $A\ ^2\Pi$ state of ionized GaX is repulsive while the excited $B\ ^2\Sigma$ state is again bound, but with a larger r_e (equilibrium internuclear distance) value.

The calculations show large charge separation in the neutral ground state of GaF. This charge separation becomes less

TABLE 2. Comparison of experimental and calculated vibrational frequencies, anharmonicities, and equilibrium bond lengths

Molecule	Electronic states	ω_e (exp.) (cm^{-1})	ω_e (calc.) (cm^{-1})	$\omega_e x_e$ (exp.) (cm^{-1})	$\omega_e x_e$ (calc.) (cm^{-1})	r_e (exp.) (a.u.)	r_e (calc.) (a.u.)	References
GaF	$X\ ^1\Sigma^+$	622.10	592	3.286	3.1	1.774	1.802	32, 57, 69
	$^3\Pi$	663.0[a]	—	2.2[a]	—	1.747[a]	1.763	16, 17, 41, 69
		662.1[b]		1.5[b]	—	1.745[b]		
GaF^+	$X\ ^1\Sigma^+$	—	655.0	—	4.5	—	1.733	32
	$B\ ^2\Sigma^+$	—	—	—	—	—	2.072	32
GaCl	$X\ ^1\Sigma^+$	365.7	342.0	1.249	1.2	2.202	2.253	32, 55, 69
	$^3\Pi$	395.1[a]	372.8[a]	2.3[a]	—	2.141[a]	2.158	24, 28, 31, 32, 41, 69
		394.7[b]		2.3[b]		2.140[b]		
$GaCl^+$	$X\ ^1\Sigma^+$	—	390.0	—	—	—	2.157	32
	$B\ ^2\Sigma^+$	—	—	—	—	—	2.353	32
GaBr	$X\ ^1\Sigma^+$	266.70	251.0	0.83	0.7	2.349	2.385	20, 32, 41, 69
	$^3\Pi$	275.8[a]	263.9[a]	2.25[a]	—	2.290[a]	2.312	20, 27, 41, 69
		274.6[b]		2.60[b]		2.292[b]		
$GaBr^+$	$X\ ^1\Sigma^+$	—	—	—	—	—	2.337	32
	$B\ ^2\Sigma^+$	—	—	—	—	—	2.480	32
GaI	$X\ ^1\Sigma^+$	216.6	208.0	0.50	0.5	2.576	2.549	29, 32, 68, 69
	$^3\Pi$	193.8[a]	213.1[a]	2.1[a]	—	2.527[a]	2.531	27, 41, 69
		184.5[b]		2.3[b]		2.545[b]		
GaI^+	$X\ ^1\Sigma^+$	—	—	—	—	—	2.565	32
	$B\ ^2\Sigma^+$	—	—	—	—	—	2.597	32

[a]Constant corresponding to $^3\Pi_0$ state.
[b]Constant corresponding to $^3\Pi_1$ state.

important in GaI. Niessen[65] has made a Green's function calculation for GaCl. In the optical emission study, Glenewinkel-Meyer *et al.*[66] have observed a transition from $X\,^2\Sigma^+ - B\,^2\Sigma^+$ for gallium halide cations, but no vibrational structure has been resolved. These transitions were located at 3.9 eV in GaF^+, 4.1 eV in $GaCl^+$, and 3.8 eV in $GaBr^+$. These data are compared with the results of photoelectron spectra of these species. The agreement for GaF^+ is found to be rather poor, however for $GaCl^+$ and $GaBr^+$, the results from both techniques agree well. In $GaCl^+$ and $GaBr^+$, these workers have observed an additional state $C\,^2\Pi$, which could not be observed in the photoelectron spectra reported by Grabandt *et al.*[32]

2.3. Dissociation Energy

The dissociation energies of the diatomic gallium halides in the gas phase have been reported by Barrow[18] from thermochemical and spectroscopic data. He has presented the various estimates of dissociation energies for most of the IIIA group monohalides. He has made the following observations:

(1) The estimates of the dissociation energy obtained by linear extrapolation of the vibrational levels in the ground state are only, on average, about 0.7 of the true values. This has been attributed to the high degree of ionic bonding in the ground state of this group of molecules.

(2) It has been shown that in some cases similar molecular states of different molecules are not necessarily to be correlated with atomic products in the same states of excitation. This, too, has a bearing on the determination of the dissociation energy of molecules in other groups.

These calculations have been discussed in our earlier review on indium monohalides.[1]

GaF

Murad *et al.*[67] have reported the thermochemical and spectroscopic value of D_e for GaF as 5.9836 and 6.3738 eV, respectively. No further investigations for dissociation energy of GaF molecule was found in the literature.

GaCl

Spectroscopic value of dissociation energy for GaCl was reported by Barrow.[18] To the best of our knowledge no recent experimental values are found in literature. More recently Yang *et al.*[41b] have performed an *ab initio* study of the ground state of this molecule and reported the D_e values for GaCl using MRCISD, MRCISD+Q, and MRAQCC calculations as 4.97 4.98, and 5.06 eV, respectively. These values are very close to the best experimental D_e value.

GaBr

The dissociation energy for GaBr was also reported by Barrow.[18] Recently we have analyzed the fluctuation bands ascribed to the $C-X$ transition of GaBr and extrapolated the potential energy curve for the C state of GaBr. The dissociation limit of GaBr was estimated as $35\,200+200\ \mathrm{cm}^{-1}$ and this dissociation limit is expected to correspond to the decomposition of GaBr into Ga* $(^2P_{3/2})+\mathrm{Br}\,(^2\mathrm{P}_{1/2})$ with an excitation energy $825\ \mathrm{cm}^{-1}$. This yields the ground state value of D_e for GaBr as $\sim 34\,375+200\ \mathrm{cm}^{-1}$ (4.26 $+0.02$ eV) which is consistent with the best value reported earlier.[68a,68b]

GaI

Recently, Saksena *et al.*[29] determined the dissociation energy for GaI by extrapolation. They have confirmed the result of Barrow[18] that the ground state of GaI dissociates into Ga $(^2\mathrm{P}_{1/2})+\mathrm{I}\,(^2\mathrm{P}_{3/2})$ [with both the atoms in their ground state] while the $A\,^3\Pi_0$ and $B\,^3\Pi_1$ dissociate into Ga* $(^2P_{3/2})+\mathrm{I}\,(^2\mathrm{P}_{3/2})$ [with Ga in the excited state and I in the ground state]. Recently, Dutta *et al.*[40] calculated the ground state D_e using *ab initio* based MRDCI calculations from the depth of the potential well, and it is around 3.34 eV as compared with the experimental value of 3.47 eV obtained from thermochemical and spectroscopic investigations.[18]

These values of ground state dissociation energies of these diatomic molecules were also given in Gaydon[68a] and Huber and Herzberg.[68b] The values of D_e in gallium monohalides decrease as the mass of the halogen atoms increases. We recommend the value of ground state dissociation energy for these molecules given in Huber and Herzberg.[68b] The atomic dissociation products for the ground and low-lying excited states is rather ambiguous and difficult to decide, however, it is expected that the dissociation products for the low-lying excited states in most of these molecules are excited metal atom and ground state halogen.

We have also calculated the ground state dissociation energy, for all these molecules using, $D_e=\omega_e^2/4\omega_e x_e$, making use of the recent available values of the vibrational parameters and have compared it with the experimental values for D_e. A large discrepancy is observed between the extrapolated value and the experimental value for GaF, GaCl, and GaBr, but for GaI this discrepancy is small. However, this discrepancy in GaI is larger in comparison to InI.

Most recently Yadav and Singh[69,70] calculated the Rydberg–Klein–Rees potentials for the observed vibrational levels of the ground electronic state as well as low lying excited states of all diatomic gallium halides using the RKR1 code of LeRoy.[71] We have also determined the centrifugal distortion constants for the above states of GaCl, GaBr, and GaI molecules. All these values are given in Tables 3 and 4. The values of the dissociation energy reported by different authors are given in Table 5.

2.4. Ionic Character of the Bond in Gallium Monohalides

Kim and Balasubramanian[34,35] have performed *ab initio* complete active space calculations and investigated the ground and excited electronic state structures of GaCl and GaBr. They show that the ground state of GaBr has a strong ionic character with the polarity $Ga^+\ Br^-$ since the total gross population of the gallium atom is much below 3.0. The contribution of the Ga d orbital in the ground state is appreciable (0.12), indicating that the polarization effects make a significant contribution to the ionic ground state. In Sec. 2.3, it was mentioned that a large discrepancy between the ob-

TABLE 3. RKR potential energy curve and centrifugal distortion constants for the ground state $X\ ^1\Sigma^+$ gallium halides

V	G_v	B_v	r_{min}	r_{max}
$^{69}Ga^{19}F$				
0	310.3863	0.358 10	1.717 26	1.838 20
1	925.9183	0.355 24	1.679 37	1.668 17
2	1534.8783	0.352 38	1.655 05	1.927 86
3	2137.2663	0.349 51	1.636 28	1.960 54
4	2733.0823	0.346 65	1.620 76	1.990 11
5	3322.3263	0.343 78	1.607 43	2.017 65
6	3904.9983	0.340 92	1.595 68	2.043 72
7	4481.0983	0.338 05	1.585 18	2.068 72
8	5050.6263	0.335 19	1.575 65	2.092 87
9	5613.5823	0.332 33	1.566 94	2.116 37
10	6169.9663	0.329 46	1.558 90	2.139 34
11	6719.7783	0.326 59	1.551 45	2.161 88

V	G_v	r_{min}	r_{max}	B_v	D_v*1E+7	H_v*1E+14
$^{69}Ga^{35}Cl$:						
0	182.5828	2.141 334 9073	2.267 620 8867	0.149 516 0047	1.006 8433	−1.088 3955
1	545.7551	2.100 534 9629	2.319 871 5961	0.148 722 4127	1.004 8643	−1.204 1363
2	906.4304	2.073 978 0163	2.357 950 7299	0.147 928 8187	1.002 9267	−1.320 9916
3	1264.6087	2.053 275 2774	2.390 247 9993	0.147 135 2227	1.001 0301	−1.438 8913
4	1620.2899	2.035 993 2896	2.419 197 8006	0.146 341 6246	0.999 1788	−1.557 6818
5	1973.4742	2.021 020 8654	2.445 912 2800	0.145 548 0245	0.997 3730	−1.677 1907
6	2324.1614	2.007 740 3653	2.471 010 0547	0.144 754 4224	0.995 6137	−1.798 3378
7	2672.3516	1.995 766 7079	2.494 877 2039	0.143 960 8183	0.993 9030	−1.920 5006
8	3018.0448	1.984 840 7823	2.517 773 8566	0.143 167 2122	0.992 2415	−2.044 4173
9	3361.2409	1.974 778 4540	2.539 885 1867	0.142 373 6041	0.990 6255	−2.173 1205
10	3701.9402	1.965 443 3724	2.561 348 6057	0.141 579 9939	0.989 0449	−2.313 1424
11	4040.1428	1.956 731 2693	2.582 269 4647	0.140 786 3817	0.987 4699	−2.477 779 09

V	G_v	r_{min}	r_{max}	B_v	D_v*1E+8	H_v*1E+16
$^{69}Ga^{79}Br$						
0	133.1730	2.292 692 2613	2.410 057 7841	0.082 871 0070	3.220 7678	4.714 819
1	398.4270	2.253 853 1177	2.457 601 3080	0.082 566 7830	3.226 4854	4.339 748
2	662.2250	2.228 280 2435	2.491 922 7973	0.082 262 3510	3.232 3449	3.737 093
3	924.5670	2.208 165 4124	2.520 832 1851	0.081 957 6150	3.238 3067	2.890 038
4	1185.4530	2.191 242 9801	2.546 596 8471	0.081 652 4790	3.244 3255	1.772 909
5	1444.8830	2.176 478 2430	2.570 253 2430	0.081 346 8470	3.250 3605	0.377 849
6	1702.8570	2.163 296 0982	2.592 378 2569	0.081 040 6230	3.256 3651	−1.338 611
7	1959.3750	2.151 338 0753	2.613 332 1666	0.080 733 7110	3.262 2896	−3.386 325
8	2214.4370	2.140 363 0875	2.633 357 8922	0.080 426 0150	3.268 0827	−5.826 901
9	2468.0430	2.130 199 9382	2.652 628 4909	0.080 117 4390	3.273 6722	−8.375 377
10	2720.1930	2.120 721 9900	2.671 272 4878	0.079 807 8870	3.278 9626	−12.231 541
11	2970.8870	2.111 832 5356	2.689 388 5067	0.079 497 2630	3.283 7924	−16.458 372
12	3220.1250	2.103 455 8145	2.707 054 2531	0.079 185 4710	3.287 8599	−21.406 934
13	3467.9070	2.095 531 2233	2.724 332 3046	0.078 872 4150	3.290 5799	−26.622 465

V	G_v	r_{min}	r_{max}	B_v	D_v*1E+8	H_v*1E+16
$^{69}Ga^{127}I$						
0	108.1873	2.518 586 7197	2.636 773 7959	0.056 800 5461	1.570 3031	−4.771 6389
1	323.7856	2.479 354 2477	2.684 448 2828	0.056 611 6149	1.570 5351	−5.072 0981
2	538.3873	2.453 496 3018	2.718 783 5386	0.056 422 6525	1.570 8138	−5.371 2594
3	751.9873	2.433 144 9289	2.747 647 8193	0.056 233 6589	1.571 1410	−5.669 4086
4	964.5873	2.416 015 7535	2.773 325 8081	0.056 044 6341	1.571 5167	−5.968 5610
5	1176.1873	2.401 064 8089	2.796 861 7829	0.055 855 5781	1.571 9386	−6.277 8295
6	1386.7873	2.387 711 3679	2.818 836 7868	0.055 666 4909	1.572 3948	−6.625 8352
7	1596.3873	2.375 593 0925	2.839 613 4776	0.055 477 3725	1.572 8478	−7.083 7403
8	1804.9873	2.364 466 0009	2.859 436 1615	0.055 288 2289	1.573 1950	−7.774 5442
9	2012.5873	2.354 156 5903	2.878 478 6701	0.055 099 0421	1.573 1874	−8.810 2539

TABLE 4. RKR potential energy curves and centrifugal distortion constants for the $A\ ^3\Pi_0$ and $B\ ^3\Pi_1$ of gallium halides

V	G_v	B_v	r_{min}	r_{max}
***A* state of $^{69}Ga^{19}F$**				
0	331.4881	0.369 40	1.691 72	1.808 85
1	990.1281	0.366 40	1.655 34	1.858 66
2	1644.4081	0.363 40	1.632 18	1.895 35
3	2294.3281	0.360 40	1.614 45	1.926 70
4	2939.8881	0.357 40	1.599 92	1.954 97
5	3581.0881	0.354 40	1.587 55	1.981 17
6	4217.9281	0.351 40	1.576 77	2.005 89
7	4850.4081	0.348 40	1.567 23	2.029 49
8	5478.5281	0.345 40	1.558 67	2.052 20
9	6102.2881	0.342 40	1.550 94	2.074 20
10	6721.6881	0.339 40	1.543 91	2.095 62
11	7336.7281	0.336 40	1.537 48	2.116 55
12	7947.4081	0.333 60	1.531 57	2.137 07
13	8553.7281	0.330 40	1.526 13	2.157 25
***B* state of $^{69}Ga^{19}F$**				
0	331.3957	0.370 40	1.689 34	1.806 52
1	990.5957	0.367 40	1.653 03	1.856 21
2	1646.8957	0.364 40	1.629 97	1.892 73
3	2300.2957	0.361 40	1.612 40	1.923 86
4	2950.7957	0.358 40	1.598 05	1.951 85
5	3598.3957	0.355 40	1.585 88	1.977 74
6	4243.0957	0.352 40	1.575 32	2.002 11
7	4884.8957	0.349 40	1.566 02	2.025 32
8	5523.7957	0.346 40	1.557 72	2.047 60
9	6159.7957	0.343 40	1.550 27	2.069 14
10	6792.8957	0.340 40	1.543 53	2.090 06
11	7423.0957	0.337 40	1.537 40	2.110 46
12	8050.3957	0.334 40	1.531 82	2.130 41
13	8674.7957	0.331 40	1.526 71	2.149 98

V	G_v	r_{min}	r_{max}	B_v	D_v*1E+7	H_v*1E+14
***A* state of $^{69}Ga^{35}Cl$**						
0	196.9832	2.083 701 4610	2.205 285 9414	0.157 959 2239	1.024 7285	−4.972 5603
1	587.5001	2.045 188 1533	2.256 828 0674	0.156 907 5143	1.035 5571	−4.972 7932
2	973.3017	2.020 273 2364	2.294 899 0288	0.155 855 5922	1.048 7436	−4.898 4413
3	1354.2817	2.000 901 7776	2.327 559 1178	0.154 803 4546	1.064 4554	−4.742 3677
4	1730.3341	1.984 738 5510	2.357 149 2241	0.153 751 0984	1.082 8949	−4.479 8010
5	2101.3526	1.970 716 5354	2.384 742 3656	0.152 698 5208	1.104 2610	−4.126 8857
6	2467.2310	1.958 241 5166	2.410 939 1161	0.151 645 7187	1.128 6756	−3.699 2945
7	2827.8630	1.946 941 7746	2.436 117 9522	0.150 592 6891	1.156 1038	−3.374 4742
8	3183.1426	1.936 565 9132	2.460 537 4614	0.149 539 4289	1.185 8068	−3.629 1816
9	3532.9635	1.926 933 9955	2.484 385 2492	0.148 485 9353	1.215 6895	−5.539 0536
10	3877.2195	1.917 911 4900	2.507 804 0400	0.147 432 2052	1.241 0339	−11.077681
11	4215.8043	1.909 394 2204	2.530 906 7804	0.146 378 2356	1.253 4200	−22.827 272
12	4548.6119	1.901 299 1187	2.553 785 9464	0.145 324 0234	1.240 9431	−42.505 165
13	4875.5360	1.893 558 2542	2.576 519 5809	0.144 269 5658	1.191 3921	−68.370 020

V	G_v	r_{min}	R_{max}	B_v	D_v*1E+7	H_v*1E+14
***B* state of $^{69}Ga^{35}Cl$**						
0	196.7764	2.082 650 5908	2.204 303 1620	0.158 107 4935	1.029 8675	−5.175 8632
1	586.8478	2.044 160 8105	2.255 925 3317	0.157 043 5745	1.040 8025	−5.170 0967
2	972.1627	2.019 272 1702	2.294 074 3549	0.155 979 6555	1.054 4121	−5.078 9457
3	1352.5981	1.999 924 9755	2.326 815 7345	0.154 915 7365	1.070 8894	−4.894 3152
4	1728.0309	1.983 782 0985	2.356 492 7518	0.153 851 8175	1.090 4718	−4.586 4887
5	2098.3383	1.969 775 2690	2.384 180 2075	0.152 787 8985	1.113 3914	−4.174 4850
6	2463.3972	1.957 309 2597	2.410 480 2742	0.151 723 9795	1.139 7913	−3.678 1691
7	2823.0846	1.946 011 4333	2.435 772 9898	0.150 660 0605	1.169 6354	−3.303 7970
8	3177.2774	1.935 629 5092	2.460 318 5375	0.149 596 1415	1.202 0664	−3.608 0682
9	3525.8528	1.925 982 6640	2.484 306 1967	0.148 532 2225	1.234 6697	−5.833 0136
10	3868.6877	1.916 935 4545	2.507 880 4788	0.147 468 3035	1.262 0639	−12.212 9860
11	4205.6591	1.908 382 7503	2.531 156 2609	0.146 404 3845	1.274 8381	−25.556 578
12	4536.6439	1.900 240 4713	2.554 228 1196	0.145 340 4655	1.260 1337	−47.445 270
13	4861.5193	1.892 439 6029	2.577 176 4081	0.144 276 5465	1.205 5986	−75.328 471

TABLE 4. RKR potential energy curves and centrifugal distortion constants for the $A\ ^3\Pi_0$ and $B\ ^3\Pi_1$ of gallium halides—Continued

V	G_v	r_{min}	R_{max}	B_v	D_v*1E+8	H_v*1E+14
***A* state of $^{69}Ga^{79}Br$**						
0	136.7615	2.234 971 4774	2.350 846 2146	0.087 116 0032	3.568 5170	−1.766 7833
1	407.8605	2.198 273 9571	2.362 767 9539	0.086 577 1932	3.618 9424	−1.771 3327
2	675.5875	2.174 514 0513	2.399 983 9725	0.086 038 1692	3.685 9594	−1.746 9862
3	939.7745	2.156 008 0444	2.436 304 2359	0.085 498 8353	3.770 9415	−1.690 1640
4	1200.2535	2.140 524 3047	2.467 499 6786	0.084 959 0952	3.875 5812	−1.586 4953
5	1456.8565	2.127 040 2783	2.495 811 4655	0.084 418 8532	4.001 9092	−1.432 9442
6	1709.4155	2.114 984 1292	2.522 272 3303	0.083 878 0132	4.152 0981	−1.207 6730
7	1957.7625	2.103 995 9855	2.547 465 0190	0.083 336 4792	4.329 0852	−0.900 3593
8	2201.7295	2.093 830 4226	2.571 761 1373	0.082 794 1553	4.535 6725	−0.497 7058
9	2441.1485	2.084 309 7695	2.595 418 7782	0.082 250 9452	4.775 1229	0.005 3585
10	2675.8515	2.075 299 1620	2.618 629 3403	0.081 706 7532	5.050 1587	0.579 4751
11	2905.6705	2.066 692 0808	2.641 542 6230	0.081 161 4832	5.362 5297	1.148 4549
12	3130.4375	2.058 401 4113	2.664 281 4591	0.080 615 0392	5.712 2784	1.543 5373
13	3349.9845	2.050 353 6113	2.686 950 8577	0.080 067 3253	6.097 9869	1.479 3959
V	G_v	r_{min}	r_{max}	B_v	D_v*1E+8	H_v*1E+14
***B* state of $^{69}Ga^{79}Br$**						
0	135.5859	2.236 988 2375	2.353 368 4164	0.086 941 9663	3.610 8391	−1.894 3197
1	404.2586	2.200 216 9254	2.402 849 2977	0.086 390 9562	3.666 9528	−1.893 9292
2	679.4344	2.176 423 0457	2.439 478 2431	0.085 839 8763	3.743 0362	−1.854 4496
3	930.9115	2.157 888 7141	2.470 982 2335	0.085 288 7263	3.840 9542	−1.770 7570
4	1188.5029	2.142 370 6940	2.499 614 2848	0.084 737 5063	3.962 9627	−1.622 6586
5	1441.9996	2.128 839 6726	2.526 414 2697	0.084 186 2163	4.111 8814	−1.404 4673
6	1691.2074	2.116 718 7307	2.551 970 5599	0.083 634 8563	4.290 7417	−1.084 3535
7	1935.9281	2.105 643 5675	2.576 659 9317	0.083 083 4263	4.503 6898	−0.643 2035
8	2175.9639	2.095 364 5394	2.600 745 6797	0.082 531 9262	4.754 8988	−0.055 1271
9	2411.1166	2.085 699 7265	2.624 424 7293	0.081 980 3563	5.049 3523	0.699 6419
10	2641.1884	2.076 509 8249	2.647 852 9541	0.081 428 7163	5.391 6813	1.599 9495
11	2865.9811	2.067 683 5589	2.671 160 0153	0.080 877 0063	5.785 6203	2.566 2676
12	3085.2969	2.059 128 6224	2.694 458 7184	0.080 325 2263	6.232 9070	3.385 9924
13	3298.9376	2.050 765 7260	2.717 851 3265	0.079 773 3762	6.733 3118	3.669 7375
***A* state of $^{69}Ga^{127}I$**						
0	96.4409	2.469 425 0248	2.594 847 9007	0.058 805	2.231 3503	−2.714 7348
1	285.9379	2.432 291 2838	2.651 597 6350	0.058 235	2.314 7111	−2.816 2281
2	470.8589	2.408 868 5376	2.694 940 8788	0.057 665	2.427 5607	−2.866 5362
3	650.9399	2.390 888 8282	2.733 172 5841	0.057 095	2.575 9057	−2.883 2274
4	825.9169	2.375 939 7390	2.768 735 7431	0.056 525	2.765 5006	−2.770 3981
5	995.5259	2.362 901 8748	2.802 784 6795	0.055 955	3.008 0670	−2.501 2193
6	1159.5029	2.351 133 9490	2.836 000 9365	0.055 385	3.313 4266	−1.989 9261
7	1317.5839	2.340 215 7970	2.868 851 5120	0.054 815	3.699 0444	−1.034 4007
8	1469.5049	2.329 842 6416	2.901 696 2114	0.054 245	4.186 2261	0.551 60401
9	1615.0019	2.319 773 4422	2.934 841 4257	0.053 675	4.803 4930	3.143 2161
***B* state of $^{69}Ga^{127}I$**						
0	91.6356	2.485 317 4234	2.613 951 1665	0.057 997 9405	2.384 6460	−3.113 1551
1	271.2019	2.447 241 3747	2.672 651 8038	0.057 411 1675	2.523 0011	−3.216 1754
2	445.4531	2.423 054 4732	2.717 834 8329	0.056 824 3945	2.719 5407	−3.198 3840
3	613.9194	2.404 256 3750	2.758 048 2172	0.056 237 6215	2.990 7193	−3.029 1269
4	776.2106	2.388 340 8445	2.795 854 3848	0.055 650 8485	3.354 6575	−2.509 5855
5	931.3169	2.374 117 8911	2.832 510 6473	0.055 064 0755	3.844 7315	−1.343 0864
6	1080.3081	2.360 876 3700	2.868 810 0971	0.054 477 3025	4.503 4114	0.976 6897
7	1221.2344	2.348 117 0167	2.905 353 4668	0.053 890 5295	5.398 9594	5.576 5226
8	1354.1456	2.335 438 7245	2.942 669 8639	0.053 303 7565	6.634 5716	14.487 741
9	1478.5919	2.322 477 6101	2.981 288 0277	0.052 716 9835	8.375 1099	32.002 514
10	1594.1231	2.308 865 1653	3.021 793 8590	0.052 130 2105	10.888 894	66.238 814
11	1700.2894	2.294 190 0448	3.064 893 3477	0.051 543 4375	14.639 267	131.396 35

served and extrapolated values of ground state D_e of GaF, GaCl, and GaBr is obtained, indicating that the ground states for these molecules have ionic contribution. However, no naturally occurring molecule is purely ionic bonded and we have to define a partial ionic character to denote departure from covalency.

There are several empirical expressions given in the literature[72–75] to calculate the percentage ionic character of a bond as calculated for InX molecules in our earlier review.[1] The calculated values of the ionic character for GaF, GaCl, GaBr, and GaI using the above mentioned expressions are given in Table 6. These calculations indicate that the ionic

TABLE 5. Ground state dissociation energy (eV) of gallium monohalides using different methods

Molecule	Thermochemical value (Barrow *et al.*[16])	Values based on the levels in $^1\Pi$ state[a]		Best values suggested by Barrow *et al.*[16]	Best values suggested by Gaydon[68a]	Best values suggested by Huber and Herzberg[68b]
		Extrapolated (Barrow *et al.*[16] and Saksena *et al.*[29])	Predissociation (Griffith *et al.*[23])			
GaF	5.98	6.24	—	6.24	6.10	5.98
GaCl	—	6.90	4.98 4.99[ab]	4.92	4.94	4.92
GaBr	—	4.31[f] 4.26[R]	—	4.31	4.35	4.31
GaI	—	3.94[CA] 3.20	—	3.47	3.46	3.47

[a]Symbols in table are as follows: (F) From analysis of fluctuation bands; (CA) From maximum of absorption continuum; (ab) *ab initio* values obtained from MRAQCC calculations; and (R) Recently derived value obtained from extrapolation of potential energy curve of $C\ ^1\Pi$ state.

forces make a larger contribution to the bonding in the ground state for heavier IIIA halides.

3. Microwave Spectroscopic Studies

The investigation of microwave spectra has provided a large amount of information on the structure of gaseous molecular species. In this concern, the studies of diatomic molecules are of basic interest because of the significant variations in the bonding character causing remarkable changes in molecular parameters such as electric dipole moment or nuclear quadrupole coupling constants which can be measured by microwave spectroscopy. Microwave studies on GaCl, GaBr, and GaI have been performed by Barrett and Mandel[43] while the first measurements on the microwave spectra of ^{69}GaF and ^{71}GaF were performed by Hoeft and co-workers.[44] Lovas and Tiemann[48] reported corrections to the assignment of quantum numbers made by Barrett and Mandel.[43] The new analysis resulted in more reliable hyperfine structure parameters which are in better agreement with the systematic trends in this group of molecules. Tiemann *et al.*[46] have studied the hyperfine structure with enhanced resolution in all the four isotopic species of GaCl in several vibrational states. They determined the Dunham coefficients, and nuclear quadrupole and magnetic coupling constants of the Ga and Cl isotopes. Plaffe *et al.*[49] measured the rotational transitions $J=2\leftarrow1$ of GaBr at 10 GHz and refined the coupling constants by more than 1 order of magnitude. Nair *et al.*[50] improving and extending the previous studies of the millimeter wave rotational structures of GaI, determined the rotational and potential constants of GaI. Nair and Hoeft[52] further measured the $J=3\leftarrow2$ rotational transition of GaI in the 10 GHz frequency region and derived molecular parameters for ^{69}GaI and ^{71}GaI from the analysis of the hyperfine structure. They have made some interesting intercomparisons of the available data for Al, Ga, and In monohalides, which have been already discussed in our earlier review.[1] Systematic variations in the quadrupole coupling constants in IIIA halides have been observed. Nair and Hoeft[52] have also compared the eq_0Q values of AlX with ClX, of GaX with BrX, and of InX with IX (where X=F, Cl, Br, and I) and have made an interesting observation that $q_0(\mathrm{IX})/q_0(\mathrm{InX})$, $q_0(\mathrm{BrX})/q_0(\mathrm{GaX})$, and $q_0(\mathrm{ClX})/q_0(\mathrm{AlX})$ are quite close to 5, which is the number of p electrons in the halogens in contrast to only one np electron in the metal. In fact, the ratio decreases somewhat as X changes from F to I and is the largest for $q_0(\mathrm{ClX})/q_0(\mathrm{AlX})$. Similarly a comparison of the ratio eq_0Q (XF)/eq_0Q (XI); eq_0Q (XCl)/eq_0Q (XI); eq_0Q (XBr)/eq_0Q(XI) for X=I, Br, Cl, and In, Ga, Al shows that the ratio is largest for the fluorides and decreases as we go to the heavier X. These ratios are consistent with the expectation that F will carry a larger negative charge in the metal halides than would Cl, Br, and I, and also that when X changes from Al to In or from Cl to I, the percentage contribution of the purely ionic structure would diminish. The most obvious explanation for q_0 (VII,VII)/q_0 (IIIA,VII) being large is that the additional VII group element contributes 5 electrons to the bonding region, whereas the IIIA group

TABLE 6. Ionic character for gallium monohalides

Molecules	(X_B+X_A)[a]	(X_B-X_A)[a]	Percentage ionic character				From the relation I.C.=μ/er[b]
			Hanny and Smyth[72]	Pauling[73]	Wilmshurst[74]	Batsanov and Durakov[75]	
GaF	5.6	2.4	58.56	68.56	42.86	68.40	76.698 (28.75)
GaCl	4.6	1.4	29.26	29.73	30.43	32.43	61.37
GaBr	4.4	1.2	24.24	22.83	27.27	25.02	59.47
GaI	4.1	0.9	17.24	13.57	21.95	14.96	55.12

[a]X_B is the electronegativity of the more electronegative atom B and X_A is that for the atom A.
[b]μ is the dipole moment; e is the electronic charge; r is the internuclear distance.

TABLE 7. Molecular constants of the $X\ ^1\Sigma^+$, $A\ ^3\Pi_0$, $B\ ^3\Pi_1$, and $C\ ^1\Pi_1$ states of gallium monohalides

Molecule	Electronic states	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	$\omega_e y_e$ (cm^{-1})	B_e (cm^{-1})	$\alpha_e \times 10^4$ (cm^{-1})	$D_e \times 10^8$ (cm^{-1})	$\beta_e \times 10^{10}$ (cm^{-1})	References
$^{69}Ga\ ^{19}F$	$X\ ^1\Sigma^+$	0.0	622.104	3.286	—	0.359 535	0.286 4235	0.479 94	0.103	57
	$A\ ^3\Pi_0$	33 105.50	663.000	2.180	—	0.370 900	30.00	0.4640	—	16, 17
	$B\ ^3\Pi_1$	33 427.80	662.100	1.450	—	0.371 900	30.00	0.4690	—	16, 17
	$C\ ^1\Pi$	47 365.37	540.960	8.972	—	0.363 470	48.78	0.6560	—	23
$^{71}Ga\ ^{19}F$	$X\ ^1\Sigma^+$	0.0	620.280	3.277	—	0.357 346	0.283 8035	0.4740	9.5	57
$^{69}Ga\ ^{35}Cl$	$X\ ^1\Sigma^+$	0.0	365.668	1.249	—	0.149 913	7.9359	0.100 77	2.018 173	55
	$A\ ^3\Pi_0$	29 524.47	395.130	2.278	−0.0177	0.158 485	19.17	0.1010	—	24, 28, 31
	$B\ ^3\Pi_1$	29 856.60	394.710	2.286	−0.0205	0.158 640	10.3528	0.0980	—	28, 31
	$C\ ^1\Pi$	40 261.00	120.000						—	
$^{69}Ga\ ^{37}Cl$	$X\ ^1\Sigma^+$	0.0	369.033	1.204	—	0.144 540	7.51299	9.369 32	1.841374	55
$^{71}Ga\ ^{35}Cl$	$X\ ^1\Sigma^+$	0.0	363.970	1.239	—	0.148 491	7.823 00	9.885	1.894	55
$^{71}Ga\ ^{37}Cl$	$X\ ^1\Sigma^+$	0.0	357.301	1.192	—	0.143 118	7.4020	9.4839	1.798	55
$^{69}Ga\ ^{79}Br$	$X\ ^1\Sigma^+$	0.0	266.710	0.830	—	0.082 797	3.266 77	3.245 756	—	20
	$A\ ^3\Pi_0$	28 162.53	274.310	1.560	−0.028	0.085 830	6.604 09	3.326 18	—	20, 27
	$B\ ^3\Pi_1$	28 532.92	274.980	1.600	−0.033	0.085 710	7.201 44	3.340 05	—	20, 27
$^{69}Ga\ ^{127}I$	$X\ ^1\Sigma^+$	0.0	216.600	0.500	—	0.056 895	1.8890	1.5600	—	68
	$A\ ^3\Pi_0$	25 572.21	193.820	2.090	−0.044	0.059 090	5.700	—	—	27
	$B\ ^3\Pi_1$	25 900.54	184.450	2.320	−0.750	0.0580 (B_0)	—	—	—	27
$^{71}Ga\ ^{127}I$	$X\ ^1\Sigma^+$	0.0	214.640	0.460	—	0.055 860	1.290	—	—	29, 30
	$A\ ^3\Pi_0$	25 572.21	190.670	1.510	−0.080	0.057 950	4.580	—	—	29, 30
	$B\ ^3\Pi_1$	25 900.54	183.490	2.680	—	—	—	—	—	29, 30

atom contributes only 1. However, the fact that the ratios are often significantly less than 5 shows that this simple interpretation is not totally correct.

Hoeft and Nair[54] have observed the microwave spectra of four natural isotopic species of GaCl in the frequency region 256–296 GHz in vibrational states up to $v=6$. The rotational states observed involved quantum number up to $J=34$. Finally they derived the extended set of Dunham parameters and the parameters for the Dunham potential. They also determined the values of ω_e and $\omega_e x_e$. Recently these same authors have studied the millimeter wave rotational spectra of GaF in the frequency region 250–300 GHz.[51] The analysis with high frequency rotational transitions have given improved and extended sets of Dunham molecular parameters. They also determined the Dunham constants which describe the ground state potential in the vicinity of the potential minimum. No observable breakdown of the Born–Oppenheimer approximation for the two isotopic species of GaF has been noticed in the limits of experimental errors, as observed for the InF, InCl, and TlF molecules. Most recently, Lenthe *et al.*[57] have performed DFT calculations to evaluate nuclear quadrupole coupling constants of a number of diatomic metal halides including GaX molecules. The ground state molecular constants obtained from the recent microwave studies are given in Table 7, whereas the recent values of the nuclear quadrupole coupling constants are given in Table 8.

4. Properties of Low-Lying Excited States

The general behavior of spectrum of gallium monohalides is very similar to one described for indium monohalides.[1] In the five excited bound Ω state ($^3\Pi_0^-$, $A\ ^3\Pi_0^+$, $B\ ^3\Pi_{1,}\ ^3\Pi_2$, and $C\ ^1\Pi_1$), only the transition from $A\ ^3\Pi_0^+$, $B\ ^3\Pi_1$, and $C\ ^1\Pi_1$ states to the ground state are allowed (as shown in Fig. 1 in our earlier review on the indium monohalides).[1] These have been observed experimentally. The lowest triplet

TABLE 8. Nuclear quadrupole coupling constants and spin rotation constant of gallium monohalides

Spectroscopic constants	$^{69}Ga\ ^{19}F$ ($X=^{19}F$)	$^{69}Ga\ ^{35}Cl$ ($X=^{35}Cl$)	$^{69}Ga\ ^{79}Br$ ($X=^{79}Br$)	$^{69}Ga\ ^{127}I$ ($X=^{127}I$)	Reference
eQq_{Ga}/MHz	−106.52	−92.10	−86.53	−81.073	47, 49, 50, 52
	−106.29	−95.58	−87.44	−81.98	57
eQq_X/MHz	—	−13.20	105.78	−369.35	53
		−12.80	101.90	−355.40	57

excited state $^3\Pi$ and the lowest singlet excited state $^1\Pi$ of gallium monohalides correspond to the following lowest excited electronic configuration (as given for the indium monohalides):[1]

$$\sigma_1^2\sigma_2^2\pi_1^4\sigma_3^1\pi_2^1.$$

These low-lying excited states involve a single excitation $.....\sigma_3^2\pi_1^4 \rightarrow .....\sigma_3^1\pi_1^4\pi_2^1$. Dutta *et al.*[40] have analyzed the SCF–MOs to explain the decrease of the internuclear distance of GaI in the $^3\Pi$ state as compared with its ground state value. The 3σ MO is mostly composed of s orbital of Ga and p_z atomic orbitals of Ga and I. The contribution of the iodine orbitals in σ_3 is found to be larger than that of the gallium atom. On the other hand, the π_2 MO is antibonding with respect to $p_{x/y}$ orbitals of Ga and I and in the π_2 MO, the atomic orbitals of Ga contribute more than that of I. Upon $\sigma_3 \rightarrow \pi_2$ excitation, the π_2 orbital is stabilized at a shorter value of internuclear distance r_e. In addition, there is a charge transfer from iodine to gallium, which enhances the multiple bond character of the Ga–I band. As a result, the equilibrium internuclear distance r_e in the $^3\Pi$ state is shorter than that of the ground state.

4.1. The *A*–*X* and *B*–*X* Systems

The existence of the first excited states $^3\Pi$ was known in the other IIIA monohalides and these states are fairly stable for gallium monohalides, similar to In–monohalides.

4.1.1. GaF

For GaF, the $A\,^3\Pi_0 - X\,^1\Sigma^+$ and $B\,^3\Pi_1 - X\,^1\Sigma^+$ transitions give rise to electronic band systems in the spectral region 290–310 nm. The electronic spectrum in this region was first studied by Barrow and co-workers.[15–17] They observed weak violet degraded bands of two kinds, single and double headed. The Ga isotope effect in GaF has been resolved and the vibrational constants for A, $B\,^3\Pi_{0,1}$, states of ^{69}GaF are obtained. Barrow *et al.*[12] performed a rotational analysis of some bands of $A-X$ and $B-X$ electronic band systems of ^{69}GaF observed in by a mixture of Ga and AlF_3 heated to 1000 °C. The reported molecular constants are given in Table 7.

The spectroscopic constants of the ground and first excited states of gallium monohalides molecules have been calculated using the DFT with different LDA and GGA by Yang *et al.*[41] recently for the first time. The calculations were performed using eight different methods to obtain r_e and ω_e of GaX molecules and they have also estimated the mean absolute error. It has been observed that the result, obtained when GGA is not involved, is closest to the experimental values. The errors in r_e are less than 0.01 Å and the errors in ω_e are less than 50.00 cm^{-1}. Use of GGAs increase r_e by 0.03–0.12 Å and make results of ω_e smaller by 20–60 cm^{-1}. The mean absolute errors for r_e and ω_e are smaller for the ground state than for the $^3\Pi$ states. In addition, it is seen that for GaF relativistic corrections, are not essential but for GaBr and GaI scalar ZORA relativistic corrections are needed. The spectroscopic constants r_e, ω_e, T_e, and IP reported by Yang *et al.*[41] are summarized in Table 2.

4.1.2. GaCl

Patrikaln and Hochberg[11] were the first to observe the electronic spectrum of GaCl in absorption in the region 320–350 nm. Miescher and Wehrli[12,13] observed this spectrum in emission as well as in absorption and confirmed the assignment of the spectrum to GaCl. They showed that violet degraded bands seen in the region 322–347 nm belonged to two overlapping systems $A\,^3\Pi_0 - X\,^1\Sigma^+$ and $B\,^3\Pi_1 - X\,^1\Sigma^+$. They made vibrational analysis for these two systems. Levin and Winans[14] recorded the absorption spectrum of GaCl at high resolution and analyzed the vibrational structure in greater detail. They also analyzed the rotational structure of the 0–0 band of the $A-X$ as well as the 0–0 and 0–1 bands of the $B-X$ system and derived the rotational constants for these states. Bartky[19] made some corrections to the Levin and Winans[14] analysis and obtained a better agreement with the microwave data of Barrett and Mandel.[43] Recently, Mahieu *et al.*[24] recorded the emission spectrum of GaCl at much higher resolution, analyzed the rotational structure of six bands (0–0, 0–1, 0–2, 1–0, 2–0, 2–1) of the $A-X$ system, and determined the rotational constants of the states involved. More recently Saksena and co-workers[28,30] used isotopically pure ^{69}Ga and recorded the emission spectrum of ^{69}GaCl at high resolution. The bands of the $A-X$ transition are violet degraded but single headed, whereas the bands of $B-X$ transitions also violet degraded show two heads. These authors reported many new bands of the $A-X$ and $B-X$ systems with some line like red degraded bands which overlapped the known bands of $A-X$ and $B-X$ systems. Formation of a head of heads is also observed. The rotational analysis of 0–0, 1–0, 2–1, and 3–2 bands of the $A\,^3\Pi_0 - X\,^1\Sigma^+$ system and the 0–0, 0–1, and 0–2 bands of the $B\,^3\Pi_1 - X\,^1\Sigma^+$ system of ^{69}GaCl has been performed and more precise vibrational and rotational constants for the A and B states have been determined. The 0–0 band of the $A-X$ transition is overlapped strongly by the 0–1 band of the $B-X$ system, while the 1–0, 2–1, and 3–2 bands of $A-X$ transition are weak and overlapped by the 0–0 band of $B-X$ transition, therefore rotational analysis of these bands have been performed with some difficulty. The high resolution spectra study of GaCl reported by the group of Saksena[28,30] is unique due to use of monoisotopic GaCl. The recent reported molecular constants for all isotopic species of GaCl are given in Table 7.

In addition to DFT study on the ground and first excited states of gallium monohalides reported by Yang *et al.*[41] most recently an all electron relativistic calculation on the ground and valence excited states of GaCl has been performed by Yang *et al.*[41b] (by the same group) using extended internally contracted multireference electron correlation techniques. The potential energy curves of all valance states and the spectroscopic constants of the bound states are obtained. The

transition properties of the $A-X$, $B-X$, and $C-X$ transitions are predicted. Some main conclusions of their investigations are given as follows:

(i) The size–extensivity correction makes an obvious improvement in the spectroscopic constants results. The MRAQCC and other methods improve the T_e, ω_e, r_e, and D_e results. Compared with the experimental values the errors in the results of ω_e, r_e, and D_e are $\sim 4.30\ \mathrm{cm}^{-1}$, 0.01 Å, and 0.04 eV, respectively.

(ii) The lifetimes of the $A\,^3\Pi_0^+$ and $B\,^3\Pi_1$ states of GaCl are on the order of the microseconds, while that of $C\,^1\Pi_1$ state of the GaCl molecule is on the order of nanoseconds, implying that $A\,^3\Pi_0$ and $B\,^3\Pi_1$ are much longer lived states than $C\,^1\Pi_1$.

4.1.3. GaBr

The GaBr spectrum was also first observed by Patrikaln and Hochberg.[11] Miescher and Wehrli[12,13] investigated the spectra of GaBr molecule and attributed the GaBr bands lying in the region 340–360 nm to the $A-X$ and $B-X$ transitions. Savitry *et al.*[20] observed a large number of new bands of A, $B\,^3\Pi_{0,1}-X\,^1\Sigma^+$ systems and reported improved vibrational constants. Rotational analysis of the (0–0) band of the $^3\Pi_{0,1}-X\,^1\Sigma^+$ systems of GaBr has been carried out by Borkowska and Zyrnicki[22] and the rotational constants B_0 and D_0 for the involved states were obtained. The constants obtained for the ground states are consistent with the results of microwave studies. Recently Borkowska and Zyrnicki[25] reinvestigated the high resolution emission spectrum in the region 340–370 nm of GaBr excited in a hollow cathode. The previous vibrational analysis of A, $B\,^3\Pi_{0,1}-X\,^1\Sigma^+$ transition has been revised and corrected. New vibrational and rotational assignments have been proposed and improved constants for the upper and lower electronic states have been determined. The reported vibrational and rotational constants for GaBr are listed in Table 7.

4.1.4. GaI

The electronic spectrum of GaI was first studied by Miescher and Wehrli[12,13] both in emission and in absorption. The discrete bands obtained in the 380–420 nm region were attributed to two overlapping transitions, namely $A\,^3\Pi_0-X\,^1\Sigma^+$ and $B\,^3\Pi_1-X\,^1\Sigma^+$. Vibrational constants of the $A\,^3\Pi_0$, $B\,^3\Pi_1$, and $X\,^1\Sigma^+$ states were determined by Miescher and Wehrli[12,13] on the basis of band head measurements from low resolution spectra. Lakshminarayana and Sethumdhavan[21] have performed a high resolution study of $A-X$ and $B-X$ transitions of GaI. They confirmed the vibrational assignments proposed by Miescher and Wehrli[12,13] through isotopic shift measurements. The rotational constant B_0 for the $B\,^3\Pi_1$ state was estimated on the basis of the separation between the P head and the Q head taken as band origin. Reversal of degradation in a sequence and in different branches within a band result in secondary heads, several of which could not be exactly assigned in the natural GaI as both Ga isotopes contribute significantly to the spectrum. In order to facilitate vibrational and also rotational analysis, recently Saksena and co-workers[29,30] investigated the emission spectrum of single isotopic species, ^{71}GaI at moderate resolution in the 380–450 nm region of the spectrum. The spectrum of ^{71}GaI was excited using an electrodeless discharge lamp run at 160–180 W microwave power (2450 MHz) and many new bands not seen earlier were observed.

The $A-X$ vibrational scheme has now been extended to include bands involving $v'<15$ and $v''<25$. The $A-X$ system is predominantly red degraded. In the higher sequences with $\Delta v=-4,\ -5,\ -6...,\ -12$ only R heads are formed. The $B-X$ system is not as extensive as the $A-X$ system. In the $B-X$ system the main head is formed by the P branch, which also has an extra secondary head (P' head). The starting of the Q branch near the origin gives rise to a head like appearance (Q head) and later a secondary head is also formed. There is yet another head formed by the R branch. The $B-X$ band system is, in general also red degraded. More precise vibrational constants for the A, B, and X states of ^{71}GaI have been reported by Saksena *et al.*[29] Later the same group performed the rotational analysis of the 1–0, 0–0, 0–1, and 1–2 bands of the $A-X$ system and 0–0 band of the $B-X$ system. They determined the rotational constants of the A and B states by a simultaneous least-squares fit of the rotational levels of both states, keeping the ground state B value fixed to the microwave value. The small value of $(B_{v'}-B_{v''})$ and the relatively large value of $(D_{v'}-D_{v''})$ with the same sign causes the reversal of the degradation in the same band. Later on Borkowska and Zyrnicki[27] reported the analysis of the A, $B\,^3\Pi_{0,1}-X\,^1\Sigma^+$ transition of the GaI lying in the region 370–420 nm. They revised the vibrational numbering of the band heads of the $A-X$ and $B-X$ systems of ^{69}GaI reported earlier by Lakshminarayana and Sethumdhavan[21] and determined the precise vibrational constants for A, B, and X states of the ^{69}GaI using the band origin data. Borkowska and Zyrnicki[27] have also performed the rotational analysis of the 1–0, 2–1, 0–0, 1–1, 2–2, and 0–1 bands of the $A-X$ system and reported the rotational constants for the $A\,^3\Pi_0$ state. These authors also reported reversal in shading in some of the bands of the $A-X$ system. They also calculated Franck–Condon factors for the bands of the $A-X$ and $B-X$ systems. It was observed by both group (Saksena and co-workers and Borkowska and Zyrnicki) that the bands of $A-X$ system are intense and well developed, whereas the bands of $B-X$ system are of lower intensity. However, a discrepancy was observed between the molecular constants reported by Saksena and co-workers[29,30] and Borkowska and Zyrnicki.[27] The recently reported molecular constants for GaI are included in Table 7. Most recently Dutta *et al.*[40] and Yang *et al.*[41] have performed theoretical calculations for the $A-X$ and $B-X$ systems of GaI and reported some spectroscopic constants for the states involved. Dutta *et al.*[40] have performed *ab initio* MRDCI on the low lying electronic states of GaI. Relativistic effective core potentials and spin orbit operators are used in the calculation. They calculated the spectroscopic constants ω_e, r_e, and T_e

for the A, B, and X states and also computed potential energy curves of 12 low-lying states. The ground state dissociation energy of GaI has been estimated and the splitting among the Ω components of the $^3\Pi$ state are found to be small. Transition probabilities of the observed transitions $A\,^3\Pi_0 - X\,^1\Sigma^+$ and $B\,^3\Pi_1 - X\,^1\Sigma^+$ are calculated from the calculated wave functions. The $A-X$ transition has been found to have a larger transition probability than $B-X$ as expected from the experimental observations. The radiative lifetimes of the A and B states are also estimated. Yang *et al.*[41] have performed DFT (*ab initio*) calculations to determine spectroscopic constants of the ground state and excited states of all gallium monohalides diatomic molecules as described in earlier sections. The spectroscopic constants obtained from their theoretical calculation are given in Table 2.

4.2. The $C-X$ System

The $C\,^1\Pi$ state in gallium monohalides similar to indium monohalides becomes progressively less stable as the mass of the halogen atoms increases. Thus in GaF, the $C\,^1\Pi$ state is a fairly stable state and a transition from this to the ground state gives rise to an extensive band system. In GaCl, it is a very weakly bound state ($\omega_e \sim 120\ \mathrm{cm}^{-1}$). In GaBr this state has a very shallow minimum and in GaI it is a completely repulsive state. The $C-X$ system of Ga–monohalides is among the least studied and only a few references are available on the spectroscopic study of the $C-X$ system.

4.2.1. GaF

The $C\,^1\Pi - X\,^1\Sigma^+$ system of GaF consists of discrete bands lying between 205 and 220 nm. This system of GaF was initially observed in absorption by Welti and Barrow[15] and in emission by Barrow *et al.*[18] These authors also reported vibrational and rotational constants for the C state. In a recent study of GaF, Griffiths *et al.*[23] have rotationally analyzed several bands of the $C\,^1\Pi - X\,^1\Sigma^+$ system. The vibrational structure shows both red and blue shaded bands and in one of the bands the Q branch shows a double head. These results are readily explained in terms of the near equality of B'_e and B''_e and the effect of the centrifugal distortion term. The non observation of any bands with $v' > 5$ is explained as due to predissociation, though no breaking off in the rotational structure is noted.[23] The predissociation has been used to estimate the dissociation energy of GaF. The $C\,^1\Pi$ state also shows a potential hump on the order of 0.26 eV.[67]

4.2.2. GaCl, GaBr, and GaI

Miescher and Wehrli[12,13] observed red degraded bands in absorption lying in the region 240–270 nm for GaCl and fluctuation bands for GaBr in the region 287.4–266.7 nm. For GaI they could observe only a continuum at 306.5 nm corresponding to the $C-X$ transition. Vibrational analysis brings one significant features in addition to the lack of stability of the $C\,^1\Pi$ state. While the $v' = 0$ level of the $C\,^1\Pi$ state in GaCl is unaffected, the $v = 1$ level shows the effect of predissociation. In the GaBr only some fluctuation bands are observed, whose analysis forms a later chapter of the thesis and a potential curve for the $C\,^1\Pi$ state of GaBr has been constructed. For GaI the $C\,^1\Pi$ state is a completely repulsive state.

As mentioned earlier an *ab initio* study on the ground and excited states of the GaCl has been reported recently.[41b] In this report Yang *et al.*[41b] performed theoretical studies on the $C\,^1\Pi_1$ state and conclude that the potential energy curve shape and spectroscopic constants of the $C\,^1\Pi_1$ state are affected by both the size-extensivity correction and the avoided crossing rules among Ω states of the same symmetry. The $C\,^1\Pi_1$ state has a very shallow potential well ($v'_{\max} = 2$). A $^3\Sigma^+$ state is crossing with a $C\,^1\Pi_1$ state. The lifetime of the $C\,^1\Pi_1$ state of GaCl is on the order of nanoseconds.

4.3. Other Systems

Recently, a broad emission spectrum in the visible region has been observed at 460 nm in GaBr and at 500 nm in GaCl by Venkatsubramanian *et al.*[5] for the first time. No structure is seen on the low frequency side while some undulatory fluctuation bands are observed on the high frequency side of this spectrum. The authors reported that the upper state corresponding to this electronic transition is a bound singlet (and triplet) state, while the lower state is the $C\,^1\Pi$ state, which is predissociated. These transitions hold the potential to be developed into an efficient excimer laser medium, similar to the laser action obtained in the rare gas halides.

5. Rydberg States

Dearden *et al.*[33] recently reported REMPI spectra of gas phase gallium monochloride produced with laser light tuned between 330 and 430 nm. The REMPI spectra were produced by one, two, and three photon resonances with electronic states that reside between 29 500 and 80 000 cm^{-1}. These authors have assigned five Rydberg series of bands involving 20 new electronic states. A summary of the spectroscopic information known for these electronic states (Rydberg states) of GaCl is given in Table 9. The adiabatic ionization potential of GaCl was estimated as 80 540 cm^{-1} by a least squares fit of the unperturbed Rydberg state origins. This new value supports improved thermochemical calculations for GaCl and $GaCl^+$. Grabandt *et al.*[32] obtained a slightly lower value of the ionization potential (79 924 cm^{-1}) from photoelectron spectra. These bands originate from one photon resonances from the previously known $^3\Pi$ state of GaCl.

Dearden *et al.*[75b] attempted to find correspondence between the REMPI spectra of InCl and GaCl to resolve state assignment. The analogy with the Rydberg state assignments between these two molecules was found to be very limited.

To the best of our knowledge, Rydberg states for GaF, GaBr, and GaI have not been reported.

TABLE 9. Summary of the spectroscopic information for the Rydberg states of GaCl

State	λ_{origin} (nm)	REMPI mechanism	Quantum defect	$\Delta G_{1/2}$ (cm^{-1})	ν_{00} (obs) (cm^{-1})
$G(5s)^1\Sigma^+$	353.10	2+1	2.86	439	56 625
$H(5p\pi)^1\Pi$	342.06	2+1	2.77	497	58 452
$I(5p\sigma)^1\Sigma^+$	332.81	2+1	2.68	—	60 076
$J(6p\pi)^1\Pi$	428.29	3+1	2.77	386	70 027
$K(6p\sigma)^1\Sigma^+$	426.69	3+1	2.73	351	70 289
$N(4f_\alpha)$	408.15	3+1	0.06	402	73 482
$P(4f_\beta)$	407.33	3+1	0.02	409	73 629
$7p\pi\ ^1\Pi$	403.19	3+1	2.78	385	74 385
$7p\sigma\ ^1\Sigma^+$	402.06	3+1	1.70	395	74 595
$5f_\alpha$	394.59	3+1	0.08	383	76 008
$5f_\beta$	395.89	3+1	0.01	387	76 133
$8p\pi\ ^1\Pi$	391.95	3+1	2.78	402	76 520
$8p\sigma\ ^1\Sigma^+$	391.29	3+1	2.69	411	76 648
$6f$	387.08	3+1	0.01	—	77 480
$9p$	385.97	3+1	2.78	389	77 705
$7f$	383.35	3+1	0.01	399	78 235
$10p$	382.10	3+1	2.69	—	78 490
$8f$	380.34	3+1	−0.07	—	78 855
$11p$	380.09	3+1	2.81	—	78 906
$12p$	378.52	3+1	2.84	—	79 235

6. Conclusion

The four states, $X\ ^1\Sigma^+$, $A\ ^3\Pi_0$, $B\ ^3\Pi_1$, and $C\ ^1\Pi$, are reasonably well characterized for GaF, GaCl, GaBr, and GaI. However, even for these states, the potential energy curve is well understood only in the vicinity of the minima (only for energies less than 15%–20% of the dissociation energy). Although high resolution electronic spectra of some isotopically pure gallium monohalides has been analyzed, more accurate vibrational and rotational analyses are required for these molecules. The ground state rotational constants are well determined from microwave studies but the excited states need studies involving pure isotopic species for all gallium monohalide molecules.

Another controversial point still needing more study is the question of predissociation in the $C\ ^1\Pi$ state, since this state is involved in the predicted excimer laser transitions in GaCl and GaBr. The predissociating state is not well characterized.

Rydberg state information is only available for GaCl. Such studies are needed for the other gallium monohaldies. Recently, DFT calculations and other *ab initio* calculations have been performed for GaF, GaCl, GaBr, and GaI. These calculations are limited to the determination of spectroscopic constants and these values are often different from experimental values in the case of GaF, GaBr, and GaI. Therefore, the calculations need to be extended to calculate other spectroscopic constants. The accuracy of the calculation needs to be extended for GaF, GaBr, and GaI to calculate other spectroscopic constants.

The dissociation energy for the gallium monohalides has the same trend as for indium monohalides. However, to best of our knowledge, thermochemical values of D_e for GaBr, GaCl, and GaI have not been reported to date. Recently, dissociation energies for GaCl and GaBr are reported. However, more accurate and updated values for most of these molecules are required.

A more detailed study regarding UV photodissociation in GaBr and GaI is clearly needed to optimize the performance of the atomic gallium laser.

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